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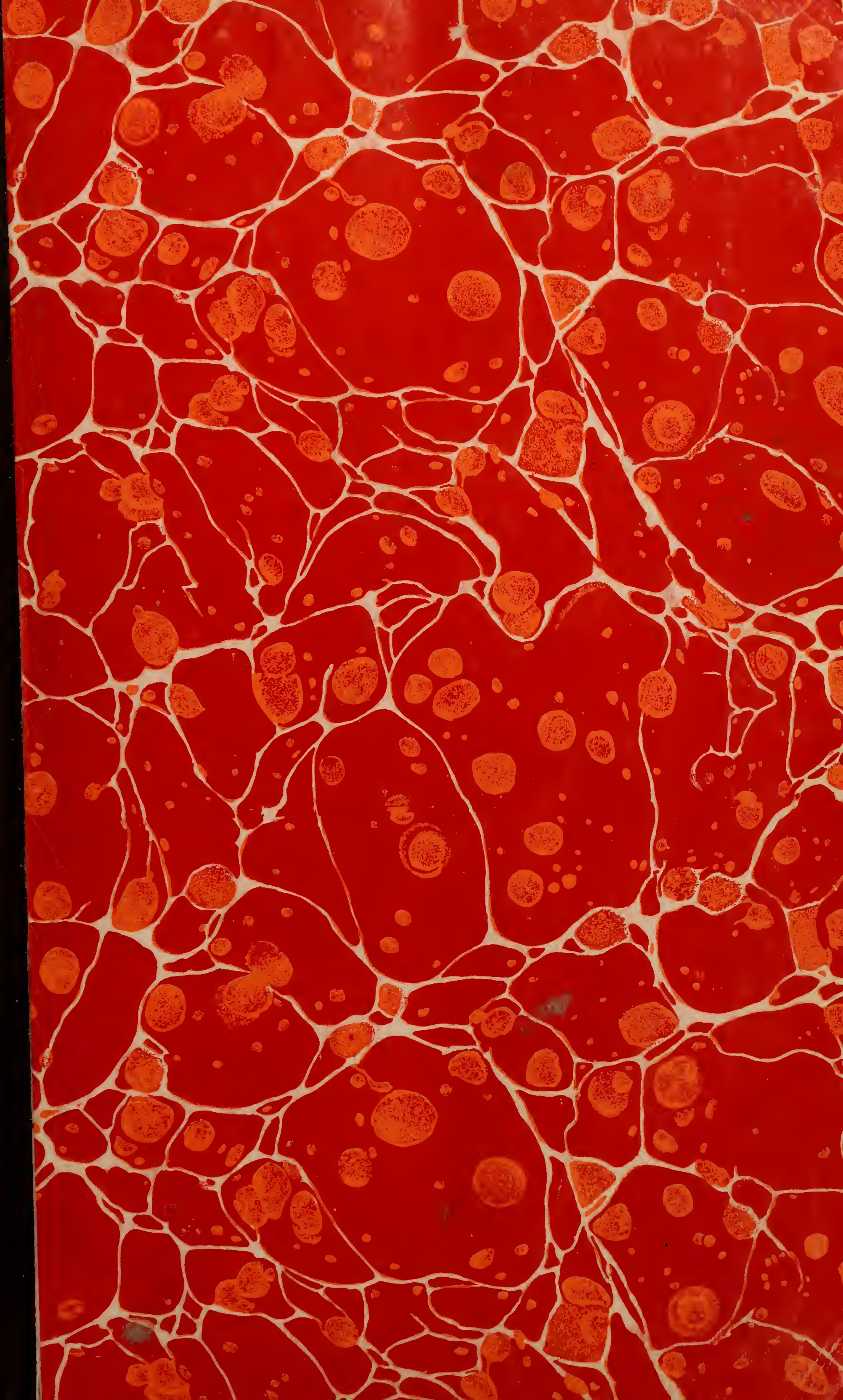

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THE PREPARATION AND CRYSTALLIZATION OF PURE ETHER-SOLUBLE RUBBER HYDROCARBON: COMPOSITION, MELTING POINT, AND OPTICAL PROPERTIES

By W. H. Smith, Charles Proffer Saylor, and Henry J. Wing

ABSTRACT

Rubber hydrocarbon from latex was purified by a method which involved the use of trypsin to remove protein adsorbed on the rubber particles. The natural antioxidants which always occur in crude rubber were used to protect the rubber during purification. The ether-soluble portion of the purified rubber was crystallized from dilute solutions at low temperatures. A special apparatus was devised for the microscopical examination of the crystalline hydrocarbon. By its means, the growth of crystals was witnessed, and the melting point and refractive indices were determined.

The crystals are spherulites composed of many fine needles. They have a consistent melting point at approximately 10° C. The refractive indices are $\epsilon=1.535$ and $\omega=1.583$ at $-5°$ C. The index of the melted crystals is 1.525 at 11° C. Assuming that the molecule contains no more than 100 carbon atoms and that the crystals are a single substance, ultimate analysis indicates that the composition is $(C_5H_8)_x$.

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I. INTRODUCTION[1]

Substantially all of the chemical and physical evidence concerning the nature of rubber is consistent with the chemical formula $(C_5H_8)_x$, and this is the generally accepted formula for "rubber hydrocarbon." An examination of the evidence discloses, however, that the above formula is not the only one which is consistent with this evidence. The difficulty of establishing beyond question the chemical composition of rubber hydrocarbon has been due largely to the lack of efficient physical methods for fractionating the hydrocarbon, of proving that the final fractions are one-component systems, and of chemically identifying these fractions. If, as seems not improbable, rubber hydrocarbon is a mixture of closely related hydrocarbons not all of which can be represented by the formula $(C_5H_8)_x$, no single method of fractionation can be relied upon to separate this mixture into its constituents. The only methods heretofore available for this purpose have been those based upon extraction with different liquids and fractional precipitation. One of the most powerful methods for fractionating a mixture of hydrocarbons is systematic crystallization and the purpose of this investigation was to develop a technic for applying this method to rubber.

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[1] The introduction is part of a note by E. W. Washburn, Phys. Rev., vol. 38, No. 9, pp. 1790–1791, 1931.

II. PURIFICATION AND CRYSTALLIZATION OF RUBBER HYDROCARBON

By W. H. Smith

1. PURIFICATION

Rubber hydrocarbon readily undergoes changes in structure of an unknown character. Light, for example, changes the viscosity of rubber solutions, and the addition of a small amount of mineral acid rapidly decreases it. Crude rubber which is used in the preparation of commercial rubber cements must be masticated before it is dissolved in organic solvents or solution may be incomplete. Busse [2] has shown that the mastication of rubber requires oxygen to produce plasticity. Pure rubber hydrocarbon quickly oxidizes when exposed to air. The natural oxidation inhibitors of Hevea rubber, two sterol-like compounds, have been isolated by Bruson, Sebrell, and Vogt.[3]

Rubber of commerce, which is obtained chiefly from the latex of *Hevea brasiliensis*, contains various other substances in addition to rubber hydrocarbon. These nonrubber materials may be classified as water-soluble, acetone-soluble, protein or other nitrogenous compounds and mineral substances. Reviews of existing methods for preparing pure rubber hydrocarbon are given by Pummerer and Koch,[4] and by Pummerer and Miedel.[5]

Some form of commercial coagulated rubber was the raw material formerly used in attempts to prepare pure rubber hydrocarbon. Pummerer and Pahl,[6] however, used latex, which is preferable to coagulated rubber because the impurities are readily attacked in an alkaline dispersion. In their method, the latex is treated three or more times at 50° C. with a 2 per cent solution of sodium hydroxide to remove protein. After each treatment, the rubber particles coalesce or "cream" in an upper layer, and the impurities in the lower layer are drawn off. At the conclusion of the third treatment, neither the biuret reaction nor the ninhydrin reaction shows the presence of nitrogen in the rubber hydrocarbon. The alkali is finally separated by dialysis. The solutions are saturated with nitrogen during purification to protect the rubber from oxidation.

The use of trypsin to remove protein qualitatively from rubber in latex was first tried by Spence.[7] Later Freundlich and Hauser [8] used it to remove protein in Hevea latex and observed microscopically the disappearance of protein adsorbed on the rubber particles.

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[2] Busse, W. F., India Rubber J., vol. 82, p. 311, 1931.

[3] Bruson, H. A., Sebrell, L. B., and Vogt, W. W., Ind. Eng. Chem., vol. 19, p. 1187, 1927.

[4] Pummerer, R., and Koch, A., Ann., vol. 438, p. 294, 1924.

[5] Pummerer, R., and Miedel, H., Ber., vol. 60B, p. 2148, 1927.

[6] Pummerer, R., and Pahl, H., Ber., vol. 60B, pp. 2152–63, 1927.

[7] Spence, D., Caoutchouc and Gutta-percha, vol. 5, p. 1632, 1908.

[8] Freundlich, H., and Hauser, E. A., Kolloid Z., 36A, Zsigmondy Festschrift, pp. 15–36, 1925.

Rubber may be separated into two fractions by ethyl ether. Petroleum ether has also been suggested for the purpose by Caspari.[9] The fractions are called, in the literature, alpha and beta, or sol and gel phases. Ethyl ether has been used in the present work, and throughout this paper the fractions are called, respectively, the ether-soluble and ether-insoluble portions of the total rubber hydrocarbon.

When crude rubber of commerce is extracted with ether, the soluble rubber is quite pure, as Feuchter[10] has indicated, and the impurities are concentrated in the insoluble portion.

According to Pummerer,[11] from 65 to 75 per cent of the total rubber is soluble in ether, and Bruson, Sebrell, and Calvert[12] reported that 75 per cent of the material was ether-soluble. They noted also that the "polymers" of rubber formed by treating it with tin tetrachloride could be separated by benzene, and that the ratio of soluble to insoluble "polymer" was 75 to 25. Whitby[13] believes that "the coincidence of these proportions was probably fortuitous." He has noted the wide variation reported in the literature on the relative amounts of soluble and insoluble rubber. The work of the Midgley Foundation[14] on the fractional precipitation of rubber indicated that unmilled pale crêpe contains a single "sol" component, which amounts to more than half of the material.

Pummerer and Koch[15] were the first investigators to report the isolation of crystalline rubber. More recently, however, Pummerer and von Susich[16] have stated that the crystallized material reported by Pummerer and Koch was not rubber but alpha gutta-percha.

In the course of work on the purification of rubber hydrocarbon by the author, several lots of pure material were prepared by the method of Pummerer and Pahl. It was observed that the treatment of latex with a 2 per cent solution of sodium hydroxide at 50° C. causes the ether-insoluble fraction to become partly soluble. At 60° C. the effect is intensified. At 80° C., however, much of the ether-soluble fraction becomes insoluble. This behavior was subsequently confirmed on isolated ether-soluble and insoluble hydrocarbon. Therefore, to separate the two fractions, it is necessary that contact with alkali at 50° C. be avoided, if a partial conversion of the ether-insoluble fraction into an ether-soluble form is to be prevented.

It appeared possible to use trypsin for the quantitative removal of protein. The enzyme mixture in technical preparations of trypsin is effective between pH 8.2 and pH 10.2. A 3 per cent aqueous solution of sodium bicarbonate provides a suitable medium, and a temperature of 38° to 39° C. is satisfactory. It was observed that if digestion of the protein in the latex takes place in the presence of a 3 per cent solution of sodium bicarbonate, the subsequent addition of sodium hydroxide equivalent to a 2 per cent solution causes creaming at room temperature. Under these conditions, the sodium hydroxide solution is used only as a creaming agent at room temperature, in accordance with DeVries and Beumée-Nieuwland's[17] technic, and the action of alkali on latex at 50° C. is avoided.

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[9] Caspari, W. A., J. Soc. Chem. Ind., vol. 32, p. 1041, 1913.
[10] Feuchter, H., Kolloidchem. Beihefte, vol. 20, p. 434, 1925.
[11] Pummerer, R., Kautschuk, vol. 2, pp. 85–88, 1926.
[12] Bruson, H. A., Sebrell, L. B., and Calvert, W. C., Ind. Eng. Chem., vol. 19, p. 1033, 1927.
[13] Whitby, G. S., Trans. Inst. Rubber Industry, vol. 5, pp. 40–62, 1930–31.
[14] Midgley, jr., T., Henne, A. L., and Renoll, M. L., J. Am. Chem. Soc., vol. 54, p. 3381, 1932.
[15] Pummerer, R., and Koch, A. See footnote 4, p. 480.
[16] Pummerer, R., and von Susich, G., Kautschuk, vol. 7, pp. 117–119, 1931.
[17] DeVries, O., and Beumée-Nieuwland, N., Arch., Rubbercultuur, vol. 9, p. 694, 1925.

With the above observations as a basis, a method of purification was developed in which it was sought to maintain unchanged the structure of rubber hydrocarbon and also to permit a sharp separation of the ether-soluble and insoluble fractions. Throughout the purification, until the coagulated rubber was extracted with acetone, the rubber hydrocarbon was protected against the action of light, which produces a gel in an ether solution of the hydrocarbon. It was also protected against the action of oxygen by the natural antioxidants, which have a powerful protective action. The antioxidants were extracted from commercial smoked sheet according to the method of Bruson, Sebrell, and Vogt.[18] An amount sufficient to keep the rubber protected was added to the latex at intervals and later removed from the coagulated rubber by extraction with acetone. The antioxidants were not isolated, but were used in concentrated alcoholic solution after freezing out phytosterol and octadecyl alcohol. The alcoholic solution of antioxidants was kept under nitrogen, to preserve their protective action.

The details of the method of purification are as follows: Four hundred milliliters of 38 per cent commercial ammoniated latex was dialyzed, using a bag of washed cellophane. According to the observation of Beadle and Stevens,[19] from 20 to 25 per cent of the total nitrogen derivatives is dialyzable, and they are consequently removed with the ammonia. Dialysis was continued until the latex was almost free from ammonia. At its conclusion, the latex, already considerably diluted, was further diluted with distilled water to a volume of 2,500 ml. About 80 g of sodium bicarbonate was added to make approximately a 3 per cent solution. The latex was warmed to 38° C. in an oven, after which a filtered aqueous solution of trypsin containing about 2.0 g was added. If the trypsin is added at room temperature, coagulation may occur. The mixture was maintained at 38° C. for 10 hours, and afterward was allowed to cool to room temperature. A solution of sodium hydroxide was added to produce a concentration of 2 per cent. Creaming commenced immediately and after one or two hours the lower layer, containing the impurities but practically free from rubber, was removed. Another portion of 2 per cent sodium hydroxide solution was added and creaming was repeated with subsequent removal of the lower layer. The number of creamings necessary to reduce the impurities to a negligible amount was estimated from the relative volumes of the upper and lower layers, by assuming that the soluble impurities were uniformly distributed between the layers at each washing. After the final washing the creamed rubber was dialyzed through a washed cellophane membrane until neutral to phenolphthalein. A portion of the rubber coagulated as the last traces of alkali were removed. The remainder was in some cases coagulated by adding acetone and passing a brisk current ofnitrogen into the mixture to cause ollision and adhesion of the rubber particles. In other cases the rubber was obtained by electrodeposition. The coagulated or electrodeposited rubber, still containing added antioxidant, was cut into strips and dried in a vacuum at room temperature. It was then cut into small pieces (2 mm ^{3}), extracted with acetone for 20 hours, and dried in a vacuum. The product was transparent and amber colored. The amount of nitrogen in the purified total rubber before extraction with acetone was found to vary between 0.008 and 0.02 per cent as determined by the Kjeldahl method. The extracted rubber was free from nitrogen when analyzed by the same method.

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[18] Bruson, H. A., Sebrell, L. B., and Vogt, W. W. See footnote 3, p. 480.

[19] Beadle C., and Stevens, H. P., Kolloid Z., vol. 13, p. 220, 1913.

The total rubber which had been extracted with acetone was subsequently extracted with ether. This operation was performed at times in a Soxhlet extractor and at other times in the apparatus suggested by Pummerer, Andriessen, and Gündel.[20] In each instance a stream of nitrogen was passed through the ether during extraction. In the course of the work it was observed that when rubber is protected by the natural antioxidant during purification, approximately 75 per cent of the total rubber is soluble in ether. The solution of rubber hydrocarbon, suitably diluted with ether, and saturated with nitrogen, was used to obtain crystalline rubber hydrocarbon. These crystallizations were not confined to one lot of material but represent rubber hydrocarbon which was purified at intervals from different shipments of ammoniated latex.

2. CRYSTALLIZATION

The conditions necessary for the formation and growth of crystalline particles have been formulated by Tammann,[21] by von Weimarn,[22] and by others. Purity is necessary, particularly freedom from material which might be adsorbed on the crystal nuclei. With rubber this means freedom from material of a nitrogenous nature. The fluidity should be high enough to provide sufficient mobility for the formation of nuclei, and the solution should be dilute in order to keep the number of nuclei at a minimum. The temperature should be sufficiently low to start the formation of nuclei and to provide a suitable medium for their continued growth.

Solutions of different concentrations of ether-soluble rubber, dissolved in anhydrous ether, were prepared and subjected to successively lower temperatures, beginning at −10° C. At −65° C., with a concentration of 1 part of rubber to 2,000 parts of ether, tiny particles of material which were birefringent under crossed nicols, separated after about one hour. The particles grew slowly and formed aggregates. These developed into larger aggregates during a period of several hours, and after about 12 hours the entire mass settled as a clot. Repeated experiments confirmed the observations. Concentrations of 1 part of rubber in 2,500, 3,000, and 3,500 parts of solvent gave similar results but with increasing slowness.

The velocity of formation of nuclei under such conditions is high and crystal habit is not established. Crystal habit is developed by using Tammann's [23] procedure, which permits the formation of only a few nuclei, and these are subsequently grown under conditions such that the formation of new nuclei is at a minimum and the velocity of crystallization is suitable.

Two Dewar flasks were used, one a silvered half-liter flask and the other of 4 liters capacity. The smaller flask was supported in the larger flask, which was inclosed in several layers of insulating felt. Each flask contained acetone at −58° C. A tube containing the ethereal solution of the rubber hydrocarbon was cooled to −65° C. for 15 minutes and then allowed to warm to −58° C., at which temperature it was immersed in the acetone contained in the smaller Dewar flask. During a 24-hour interval the temperature increased about 15°. Although the temperature rose, the velocity of crystallization was low and a satisfactory degree of supersaturation was maintained. The rubber deposited on the sides of the tube in small nodules which appeared to have developed radially from a point in the center. By maintaining suitable conditions for a longer period, nodules half a millimeter in diameter or larger are produced. Approximately 95 per cent of the rubber crystallizes at −65° when the initial concentration is 1 part of rubber in 2,500 parts of ether.

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[20] Pummerer, R., Andriessen, A., and Gündel, W., Ber., vol. 60B, pp. 1583–1591, 1928.

[21] Tammann, G., Kristallizieren u. Schmelzen, Johann Ambrosius Barth, Leipzig, 1903.

[22] von Weimarn, P. P., Zur Lehre von den Zuständen der Materie, Theodor Steinkopff, Dresden, 1914.

[23] Tammann, G., Kristallizieren u. Schmelzen, see footnote 21, p. 483.

Material prepared as nodules was used in the examination of optical properties and in the determination of the hydrogen-carbon ratio.

In addition to the crystals of ether-soluble rubber obtained as described above, crystals of the ether-insoluble form of rubber have also been produced. These latter crystals differ materially from the ether-soluble crystals both in appearance and in melting behavior. They will be discussed in a later paper.

IV. MICROSCOPICAL STUDY OF CRYSTALLINE RUBBER

By Charles Proffer Saylor

The low temperature which is necessary for the nodules of rubber hydrocarbon to be stable in contact with their ether solution makes it impossible to watch their growth or determine their properties by the usual microscopical methods. Several forms of apparatus[24] have been used in the examination of crystals at low temperatures, but, since none of them was entirely suited to the uses described in this paper, an apparatus was designed by means of which the crystallinity of the nodules was established and some properties of the crystals were determined.

1. THE APPARATUS

The apparatus which was employed is illustrated in Figure 1. It departs from that commonly used in photomicrography between crossed nicols chiefly in three particulars: (1) The sample is contained in an unusual form of cell; (2) a Dewar flask with optically plane windows at the bottom holds the cell and its temperature bath; and (3) a long range immersion condenser, capable of focusing the light source on the crystals at the bottom of the cell, is employed. The details of these parts are represented in Figure 2. The cell and Dewar are made entirely of Pyrex glass. The cell is a cylinder with an inside diamater of 12 mm and a height of 10 mm. To its polished upper and lower edges are sealed the ground and polished disks, 0.5 mm thick, which serve as windows. Two tubes for filling and emptying connect with the cylinder. One of them is bent downward inside the cell and nearly touches the surface of the bottom disk. The windows of the Dewar flask, which also are polished, optically plane disks of glass sealed to polished edges on the flask, are 1 mm thick, 30 and 24 mm, respectively, in diameter, and 1 mm apart. When the cell rests on the inner window of the Dewar flask, the distance from the crystals on its bottom to the outside of the flask is 3.5 mm. Therefore,

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[24] Such apparatus is reviewed by E. M. Chamot and C. W. Mason, Handbook of Chemical Microscopy, vol. 1, pp. 206-208, John Wiley & Sons (Inc.), New York, 1930.

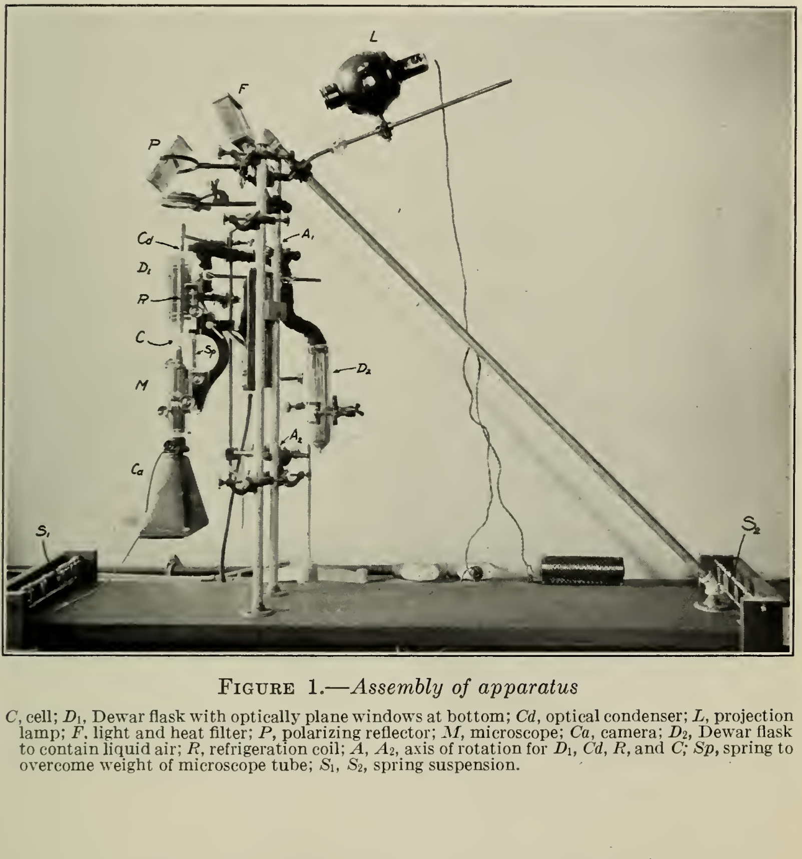

Figure 1.—*Assembly of apparatus*

C, cell; D_1, Dewar flask with optically plane windows at bottom; *Cd*, optical condenser; *L*, projection lamp; *F*, light and heat filter; *P*, polarizing reflector; *M*, microscope; *Ca*, camera; D_2, Dewar flask to contain liquid air; *R*, refrigeration coil; *A*, A_2, axis of rotation for D_1, *Cd*, *R*, and *C*; *Sp*, spring to overcome weight of microscope tube; S_1, S_2, spring suspension.

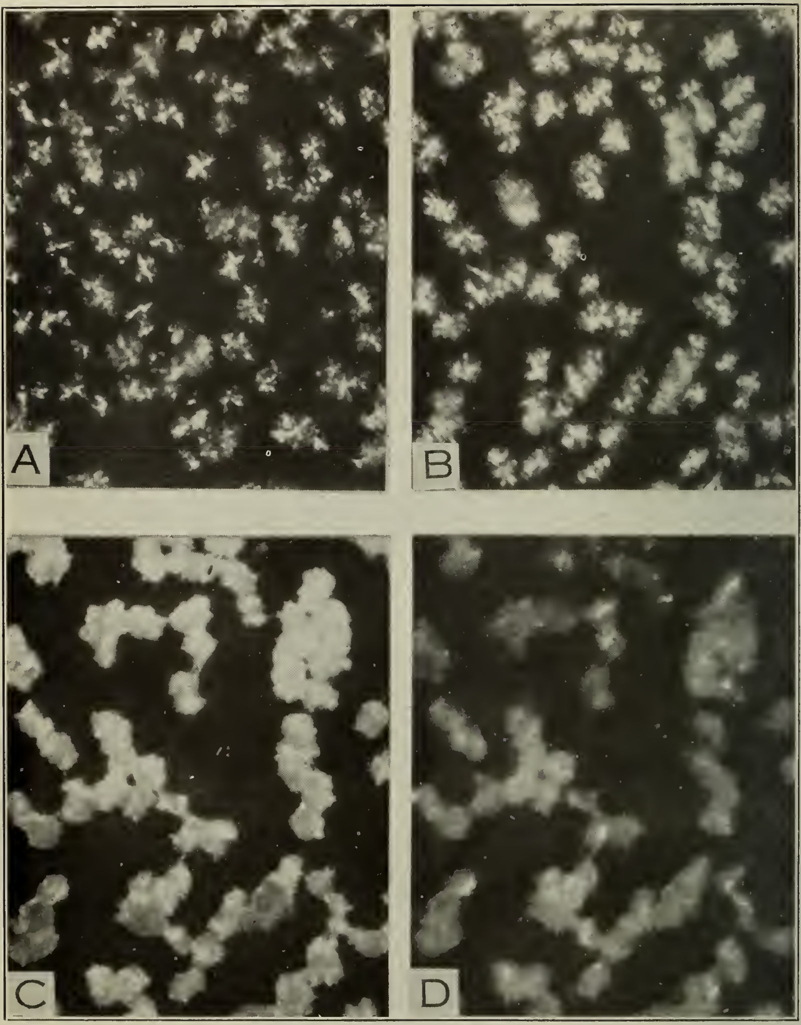

FIGURE 3.—*Photomicrographs showing melting of ether-soluble hydrocarbon crystals*

A, crossed nicols. × 200. Rubber crystals surrounded by mother liquor. They are roughly spherular clusters of birefringent crystals. The brightness of the clusters is created by their optical anisotropy. Temperature, −50° C. Exposure, 1 second.

B, crossed nicols. × 200. A similar field after the mother liquor has been withdrawn. Otherwise, except for optical distortion produced by the adhering liquid, there is no significant difference. The different clusters can be seen in the same position in this and succeeding photomicrographs. Temperature, −45° C. Exposure, 5 seconds.

C, crossed nicols. × 200. Same field as *B*. The ether has all been evaporated by suction. Surface tension has distorted the crystals. As a consequence the brightness of birefringence is less. This is indicated by the greater exposure. Temperature, −40° C. Exposure, 12 seconds.

D, crossed nicols. × 200. Same field as *B*. Just below the melting point. The principal difference between this and *C* arises from differences in the photomicrography. Temperature, +8.4° C. Exposure, 12 seconds.

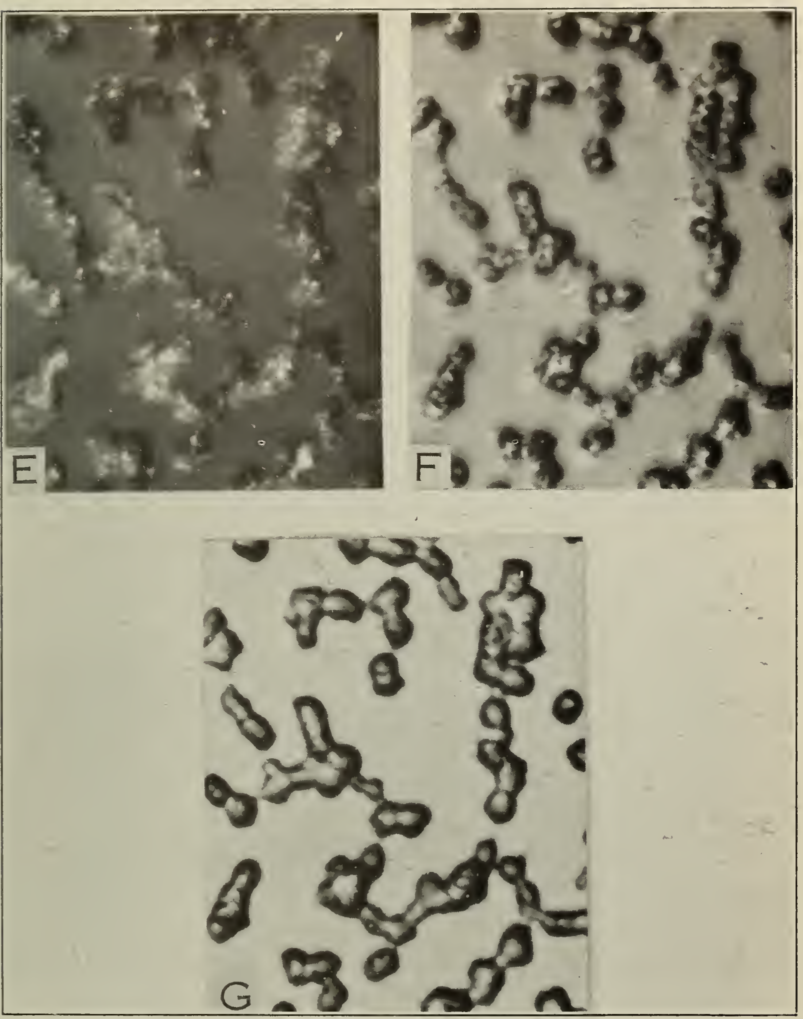

Figure 3 (Continued).—*Photomicrographs showing melting of ether-soluble hydrocarbon crystals*

E, crossed nicols. × 200. Same field as *B*. Much of the birefringence has disappeared. It is supposed that the more severely distorted crystals have melted below the true melting point. Those which were less distorted persist unchanged. Temperature, +9.7° C. Exposure, 12 seconds.

F, crossed nicols. × 200. Same field as *B*. Very long exposure so that extinct field appears bright. Birefringence has disappeared. Groups are beginning to flow into globules. Temperature, +11.8° C. Exposure, 1 minute.

G, parallel nicols. × 200. Same field as *B*. Because of the smallness of the clusters, the surface tension forces have been relatively large. Melted ether-soluble rubber hydrocarbon has flowed into rounded globules. Temperature, +12.6° C. Exposure, 1/10 second.

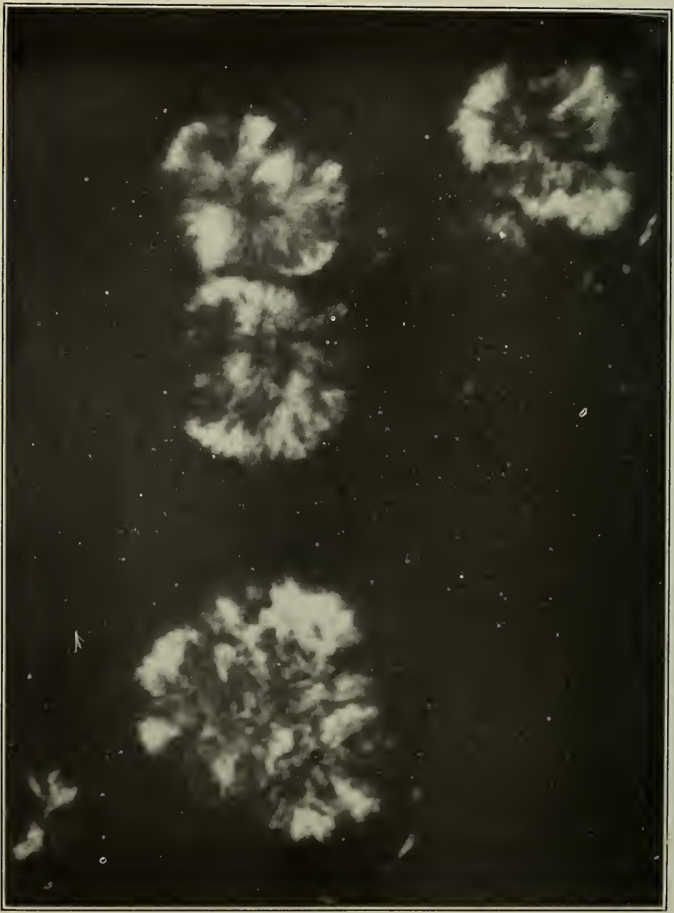

Figure 4.—*Crystals of ether-soluble rubber hydrocarbon*

Crossed nicols. × 500. The dark cross which is characteristic of spherulites can be readily observed.

although the crystals were viewed at temperatures as low as −90° C, it was possible to use a 16 mm objective, N. A. 0.25. An excessive amount of glass intervened between the objective and its focal plane, but satisfactory images were formed despite this handicap. The Dewar flask contained acetone, which was cooled by drawing liquid air from flask, D_2 in Figure 1, through the coil, *R*, of copper tubing. Temperatures were determined by means of a triple junction, copper-constantan thermocouple. The condenser, *Cd*, was so designed that it focused the entire beam from the projection lamp upon the preparation, forming an image the size of the microscope field. The microscope, a petrographic model with a rotating tube analyzer, was bolted by its base to the vertical support. A rotation of 90° at the pillar joint permitted complete inversion of the instrument. Except when refractive indices were determined, a multiple plate polarizer served as the primary nicol. A tube camera with side telescope was used both for viewing and for photographing preparations in th ecell. The positions of the Dewar flask, the condenser, and the coils of copper tubing were adjusted on a swinging support so that they were coaxial with the microscope when the support was pushed against stops and clamped.

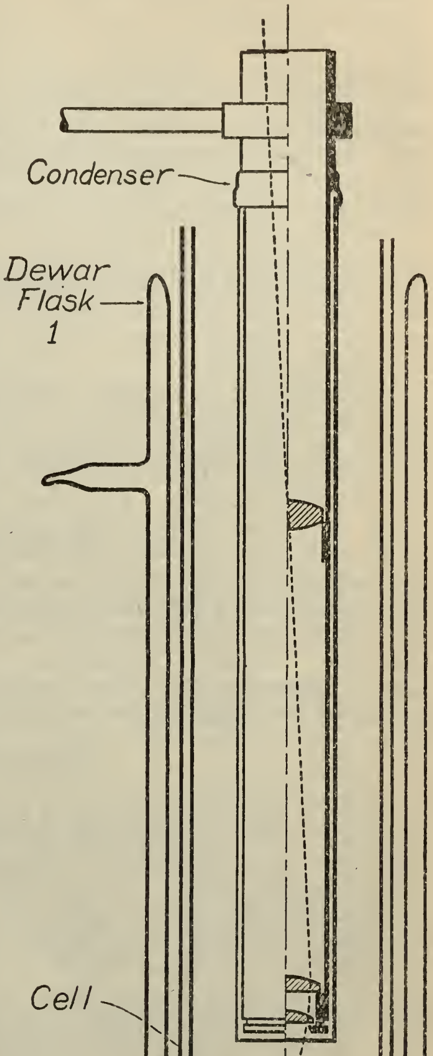

FIGURE 2.—*Cell, Dewar flask, and condenser*

The dotted line indicates the course of a beam of light. It intersects the center line at levels where images of the arc crater are formed

2. THE CRYSTALS OF ETHER-SOLUBLE RUBBER HYDROCARBON

A solution of ether-soluble rubber hydrocarbon was treated as has been described on page 483. This treatment caused the formation of nodules on all walls of the cell. More nodules formed on the bottom of the cell, however, than on any of the other surfaces. If the cell was removed from the bath, the upper surface touched briefly with a finger, and the cell replaced in the bath, the temporary warmth caused the crystals at the spot touched to dissolve but did not disturb those on the bottom of the cell. The alcohol in the Dewar flask was cooled to −50° C. The cell was transferred to the flask, and the revolving carriage which supports the Dewar flask, cooling coil, condenser, and cell was swung into the optical axis of the microscope. Viewed between crossed nicols, the crystals appear as in Figure 4.[25] They are spherulites, clusters of thin needles radiating from a central point. By the birefringence of its individual needles, the cluster appears bright against the dark background. The best organized clusters tend to show the typical spherulitic extinction, a dark radial cross, the arms of which are parallel to the nicol prisms and rotate with them, but in general this phenomenon is not very well marked. This may be caused either by a low state of organization in the clusters or by the needles not having parallel extinction. It has been mentioned on page 483 that the latex used in this work was obtained in several different lots. The appearance and properties of the spherulitic clusters did not depend upon the sample of ammoniated latex from which they had been prepared, although the conditions of crystal growth modified the size of the individual needles and their arrangement in the cluster.

Birefringence, or optical anisotropy, is characteristic of three different conditions of matter: (*a*) Viscous liquids or colloidal materials are birefringent when under mechanical strain. Thus a sheet of transparent rubber shows polarization colors when stretched between crossed nicols. This phenomenon is fundamentally different from that described in this report. Furthermore, the conditions under which the clusters were formed are unlikely to result in strains. (*b*) Liquid crystals are birefringent. The great amount of structure observable shows that the clusters of Figure 4 are not liquid crystals. (*c*) The crystals of five out of six systems of true crystals are birefringent. The crystals of rubber hydrocarbon undoubtedly belong to one of these groups. They are true crystals and appear to offer a means of purifying rubber hydrocarbon.

3. MELTING POINT

When a birefringent crystal melts, the birefringence disappears abruptly when the structural interrelations of the solid are loosened and before the first signs of flowing can be observed.

The mother liquor was removed from a preparation of rubber crystals and all residual solvent evaporated by evacuating the cell. The photomicrographs in Figure 3 illustrate the changes in these crystals as they became warmer and establish the melting point of the rubber crystals as higher than +9.5° C. and lower than +11° C. The melting point appeared to be independent of the sample of latex and also not to vary with different preparations of crystals. The conditions of determining the melting point influenced the result somewhat, but not more than would be expected. Table 1 indicates the results of a varying group of such determinations.

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[25] An earlier photomicrograph of sol rubber crystals was published with the note previously mentioned (see footnote 1, p. 479).

TABLE 1.—*Determinations of the melting point of ether-soluble rubber hydrocarbon*

Melting point (° C.)	Conditions affecting accuracy
9.5	Evaporation of ether with water-jet pump.
9.8	Evaporation of ether with an oil pump.
9.5–11	Very thorough removal of solvent. Evacuation with oil pump continued during entire time that temperature rose. A series of photomicrographs (fig. 3), shows the condition of the crystals at each significant temperature.
9.0–9.5	Replacement of ether with acetone. Melting of crystals determined under acetone.
8.0–8.8	Replacement of ether with acetone. Replacement of acetone with Sonstadt's solution [1] diluted with acetone. Melting was determined under this mixture in which the crystals had been immersed at a temperature near their melting point for 4 days.

[1] Sonstadt's solution, otherwise known as Thoulet's solution, is a saturated water solution of potassium mercuric iodide. It is used for gravity separations of minerals and occasionally for the determination of refractive indices.

NOTE.—The second and third determinations are believed to be more trustworthy than the others. The third is particularly favored because of the thorough removal of the solvent (the oil pump operated about 3 hours) and because the making of photomicrographs largely removed the personal element from the determination.

That fraction of rubber hydrocarbon which is soluble in ether is therefore a stable liquid at the ordinary temperatures at which rubber is used. Its melting point has not seemed to depend upon whether it represented the whole ether-soluble component or only that which remained in ether solution after a portion had been precipitated with acetone and discarded.

4. OPTICAL PROPERTIES

The largest spherulites which have so far been grown for microscopical examination were about 50 microns (0.05 mm) across. In these clusters the individual particles were needles about 20 μ long and 1 or 2 μ wide.

The refractive indices of the crystals were determined by immersion [26] in aqueous solutions of potassium mercuric iodide. The method of central illumination was used to indicate the relation between the index of a crystal and the immersing liquid. By adjusting concentrations of the iodide solutions each index of the crystals was matched at $-5°$ C. The index of the corresponding liquid was then determined on an Abbe refractometer at the same temperature.

So far as possible, needles were chosen which were somewhat separated from the clusters. Two indices were determined corresponding to the ϵ and ω of uniaxial crystals. It must not be inferred, however, that the rubber crystals are uniaxial. There was no attempt to obtain an interference figure.

The uncertainty of the determinations is greater than equally careful work would yield in ordinary optical determinations. It is believed to be about ± 0.003. The indices found are

$$\epsilon = 1.535 \text{ at } -5° \text{ C.}$$
$$\omega = 1.583 \text{ at } -5° \text{ C.}$$

Determinations of the optical character of elongation were made with the Johannsen wedge. The crystals have negative elongation. This is consistent with the determined values for ϵ and ω.

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[26] For a description of the immersion method, the reader is referred to F. E. Wright, The Methods of Petrographic-Microscopic Research, pp. 83 et seq., Carnegie Inst. Washington Pub. 158, Washington, D. C., 1911, or to Albert Johannsen, Manual of Petrographic Methods, 2d ed., pp. 271–275, McGraw-Hill Book Co., New York, 1918.

The temperature was allowed to rise and the refractive index of the rubber was determined after the crystals had melted. The refractive index of melted ether-soluble rubber hydrocarbon crystals was found to be 1.525 at 11° C. This corresponds closely with the value found by McPherson [27] who used large samples of total rubber hydrocarbon.

The microscopical examination of the crystals of rubber hydrocarbon indicates that they are spherulites composed of many fine needles. They have a consistent melting interval of narrow range. The refractive indices of the crystals have been determined. They are higher than the index of the rubber after melting by an amount inconsistent with the "melting" of liquid crystals, but consistent with the melting of true crystals.

V. DETERMINATION OF THE COMPOSITION OF PURE ETHER-SOLUBLE RUBBER HYDROCARBON

By Henry J. Wing

The ratio of hydrogen to carbon in rubber and rubber hydrocarbon has often been determined. Upon these determinations, in large part, has rested the assumption that rubber hydrocarbon is a polymer of isoprene, which may be represented as $(C_5H_8)_x$. However, this assumption is not entirely justified because of the questionable purity of the substances analyzed and the low precision of many of the reported results. The preparation of pure rubber hydrocarbon in this laboratory offered opportunity to make an accurate determination of the ratio of hydrogen to carbon by the usual method of organic combustion.

1. APPARATUS

The combustion furnace and accessories (Fig. 5) were similar to those described by Bruun [28] except that all mercury seals and flow meters were eliminated and all but two of the joints beyond the preheating furnace, *A*, were hermetically sealed. These two, *C* and *D*, were sealed on the outside with DeKhotinsky cement so that the gas stream did not come in direct contact with the cement. In order to obtain suitable blank runs it was found necessary to run the preheating furnace, *A*, at a higher temperature than that of the combustion furnace, *B*.

The absorption tubes were two 75 mm Schwartz U tubes fitted with ground joints on the side arms so that no rubber connections were used. In order to avoid loss due to the action of hot water on the greased joints, the exit tube, *E*, from the combustion tube was bent in a U and a small bulb was blown on the outflow side of this U. Most of the water from the combustion condensed in the bend of the U. The oxygen was allowed to pass until all this water was transferred to the weighing tube in the form of vapor. The weighing tubes were weighed filled with dry hydrogen both before and after the combustion. This made any correction for air buoyancy unnecessary.

A silica-glass sample tube was used in making the combustions instead of an open boat in order to prevent too rapid burning of the rubber. One end of the tube was open and unconstricted. The other end was closed except for a pinhole of such size that the rubber

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[27] A. T. McPherson, B. S. Jour. Research, vol. 8 (RP449), p. 757, 1932, plots the refractive index of purified rubber against temperature. The refractive index interpolated from that curve is 1.5236 at 11° C.

[28] E. W. Washburn, J. H. Bruun, and M. M. Hicks, B. S. Jour. Research, vol. 2 (RP45), p. 487, 1929.

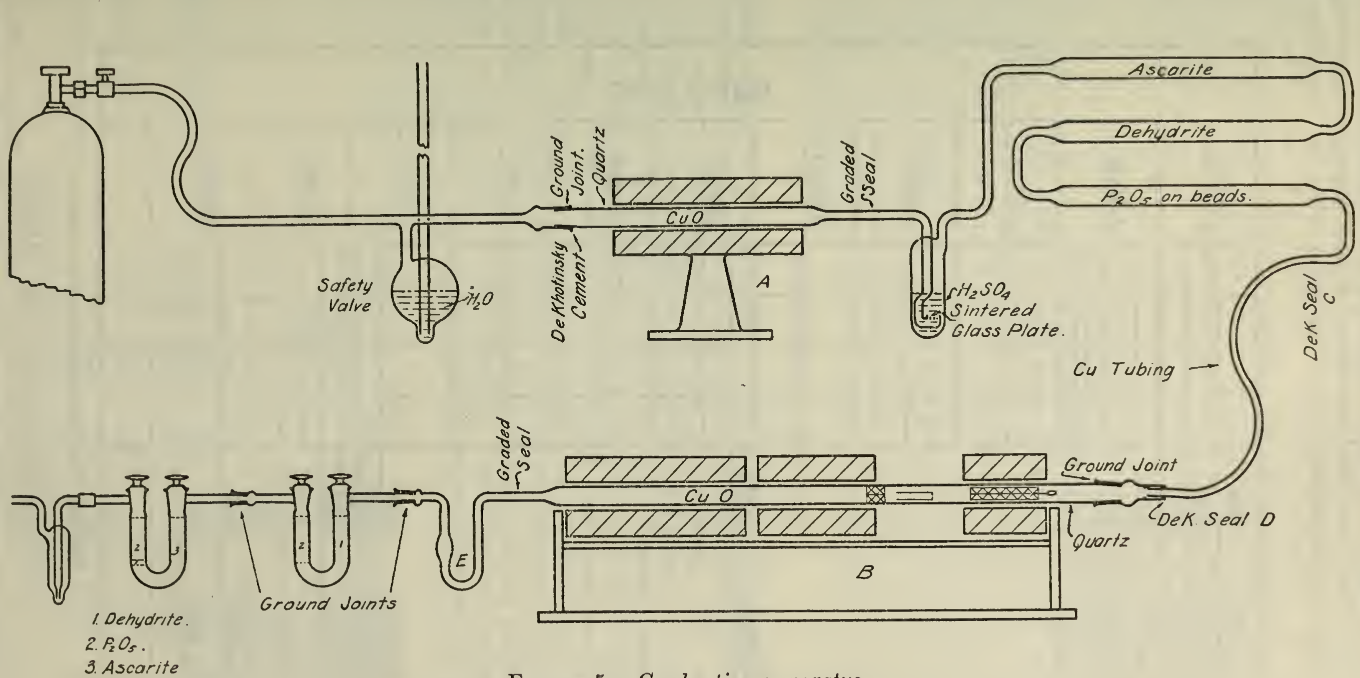

FIGURE 5.—*Combustion apparatus*

solution would not run through, yet in the combustion furnace oxygen could enter. This tube had two small hooks near the open end so that it could be suspended by a platinum wire for weighing and handling.

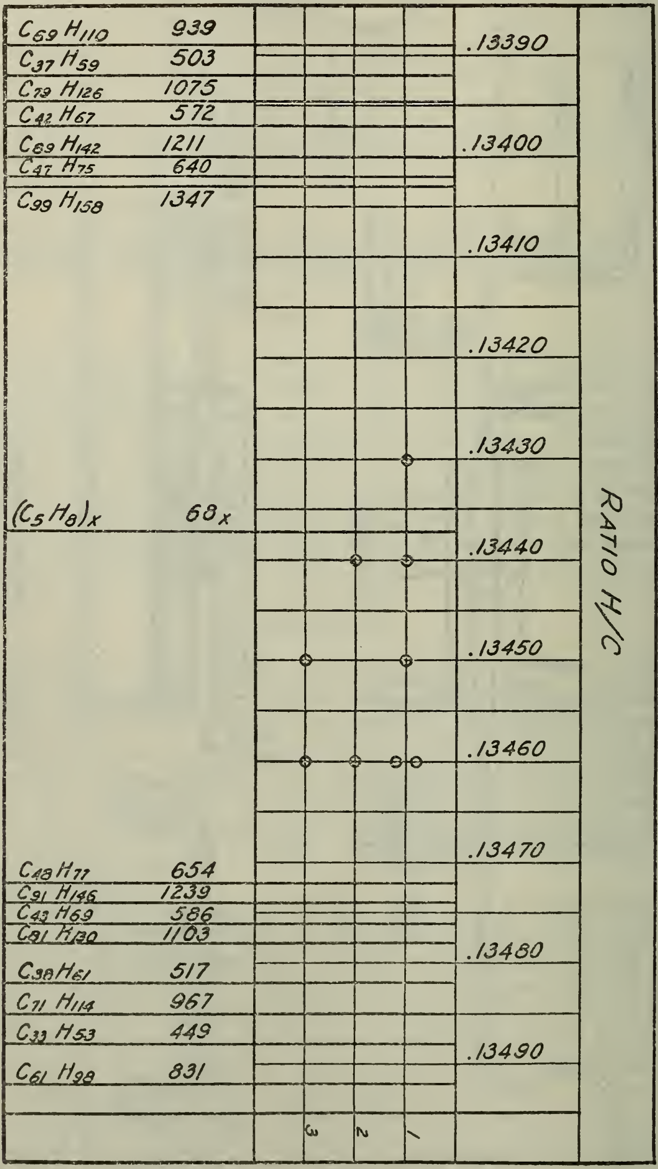

FIGURE 6.—*Hydrogen-to-carbon ratios*

2. PREPARATION OF THE SAMPLE

The material for analysis had been purified as described in the first part of the paper and put into ether solution. A small portion of this solution was placed in the sample tube. The ether was evaporated from this first small quantity of rubber solution by placing the sample tube containing it in a wide test tube and carefully reducing the pressure. This procedure was repeated until about 0.2 g of the hydrocarbon had been collected. In order to remove the last traces of solvent the sample tube was then placed in a small glass chamber which was heated to about 100° C. by a glycerol bath and which was evacuated to a low pressure by a mercury vapor pump. The sample was evacuated about 18 hours, then transferred to the balance case and, after standing about 20 minutes, was weighed.

3. BALANCE, WEIGHTS, AND WEIGHING

All weighings were made on a high grade analytical balance sensitive to 1/20 mg. The weights used were calibrated by the weights and measures division of this bureau, and the necessary corrections were applied. The blank runs were reproducible to 0.1 mg. Vacuum corrections were made on the weight of the sample, assumed to have a density 0.9 g/cm^3. However, this has no effect on the carbon-to-hydrogen ratio. Assuming that all the weighings were made to ±0.1 mg, then the maximum possible relative error in the percentages of hydrogen and carbon, and in the ratio of hydrogen to carbon would be ±0.2 per cent.

4. ANALYTICAL RESULTS

Three different preparations of the ether-soluble rubber hydrocarbon, purified as described in Section II of this paper, were analyzed and the ratio of hydrogen to carbon determined. The results are given in Table 2 and are shown graphically in Figure 6. These results are members of a continuous series from which the only omissions were those in which the absorption tubes failed to function either because of stoppage or channeling. Many blank runs were made with the furnace. These were continued until the difference in successive weighings under the conditions of an actual determination was not more than ±0.1 mg. The final ratio of hydrogen to carbon is independent of the weight of the sample. However, as a check on the result the weight of the sample and the percentages of carbon and of hydrogen were determined.

TABLE 2.—*Determination of the ratio of hydrogen to carbon*

	Hydrocarbon taken	H_2O absorbed	CO_2 absorbed	Hydrogen found	Carbon found	H/C ratio
	g	*g*	*g*	*Per cent*	*Per cent*	
Original preparation	0.2009	0.2127	0.6481	11.84	87.98	0.1346
	.2328	.2462	.7516	11.83	88.05	.1344
	.2598	.2732	.8345	11.77	87.66	.1343
	.2358	.2496	.7606	11.84	87.97	.1346
	.2320	.2450	.7475	11.82	87.87	.1345
Crystallized once	.2107	.2232	.6799	11.85	88.01	.1346
	.2390	.2525	.7709	11.82	87.97	.1344
Crystallized three times	.1365	.1448	.4417	11.87	88.25	.1345
	.2373	.1349	.4111	11.86	88.07	.1346

These results are figured on the ash-free basis. In every case the ash content was less than 0.1 per cent, practically at the limit of the accuracy of the weighings. The difference between the sum of the hydrogen and carbon percentages and 100 per cent is probably due to the presence of oxygen. Some of the samples were exposed to the air longer than others, which may account for the difference in the sums.

The first step in the interpretation of these results should be the determination of the number of possible compounds which, if subjected to combustion analysis, would give results somewhat in accord with those found.[29]

If we assume for simplicity that the compound does not have more than 100 carbon atoms in the molecule, then the number of possible compounds may be confined to reasonable limits. The ratio of hydrogen to carbon in isoprene or any of its isomers or polymers is 0.13437 based on the International Table of Atomic Weights for 1932. A number of hydrocarbons are possible having less than 100 carbon atoms in the molecule and a ratio of hydrogen to carbon very near to that of the $(C_5H_8)_x$. The diagram (fig. 6) shows all the possible hydrocarbons in this region. The horizontal scale represents ratio of hydrogen to carbon. Each of the labeled vertical lines represents an individual hydrocarbon. The groups of points in circles represent analyses of different preparations of the ether-soluble rubber hydrocarbon. Group 1 shows the results of analyses of the purified hydrocarbon; group 2, material which had been crystallized once; and group 3, that which had been crystallized three times.

The distribution, in the neighborhood of the C_5H_8 and its polymers, of the hydrocarbons having less than 100 carbon atoms, is fortunately unique. It so happens that none of these hydrocarbons has a ratio of hydrogen to carbon very close to that of C_5H_8 as is shown in Figure 6. The difference in the ratio of the nearest hydrocarbon on either side of C_5H_8 is $0.13472-0.13403=0.00069$. This offers the possibility of identifying the rubber hydrocarbon as a polymer of C_5H_8 provided it has less than 100 carbon atoms in the molecule and that the analysis is of the required accuracy. If, however, the molecule contains more than 100 carbon atoms, there still remains the possibility that it may not be a polymer of C_5H_8. Only reliable molecular weight determinations can decide this question.

At present it is not possible to say definitely that the rubber hydrocarbon has a molecule of less than 100 carbon atoms. However, the fact that the material as prepared and used in this laboratory crystallizes readily indicates that the molecule is possibly much smaller than has been frequently assumed.

V. ACKNOWLEDGMENTS

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[29] E. W. Washburn, B. S. Jour. Research, vol. 4 (RP145), p. 221, 1930.